B

THE OCCURRENCE OF NORMAL NONANE IN THE VOLATILE OIL OF SAROTHRA GENTIANOIDES L.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in the
Faculty of Pure Science of
Columbia University.

By
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NEW YORK CITY
1932

To My Wife,
Bessie King Marion

ACKNOWLEDGMENT

The following investigation was made possible through the kindness of Professor Marston T. Bogert, and was carried out under his direction. It gives me great pleasure to express my sincere appreciation for the assistance and friendly advice from him during the investigation.

The author also wishes to express his thanks to Professor C. C. Curtis, of the Department of Botany, of Columbia University, and to Professor C. M. Yoder, Department of Biology, Lenoir Rhyne College, for their kindly assistance in identifying the plants used in this investigation.

Special acknowledgment is made here also to the Head of the Physics Department of Columbia University for the use of a Polariscope, and to Professor E. E. Randolph, of the North Carolina State College, for the loan of a Refractometer.

For all other assistance received during the course of this investigation, and not specifically acknowledged in the main body of the text, the author desires at this point to express his sincere thanks.

PREFACE

The enormous development of synthetic organic chemistry in recent years has, in a measure, over-shadowed the study of naturally occurring organic compounds and plant products. This is particularly true of organic medicinals and dyes where coal-tar products have replaced so many of the natural remedies and colors generally in use a few decades ago.

In spite of the fact that the field of phytochemistry offers broad opportunities for research, even a cursory examination of the literature reveals that in this country particularly very few men care to engage in this line of investigation. This may be explained partly on the basis that the collection of material for an investigation is largely seasonal, tedious, and expensive, as compared with the readily obtainable supplies of most coal-tar products.

In the special field of Essential Oil Chemistry there are indeed very few workers in this country. Germany and France have been pioneers in this field, and the work that has been done in America is largely traceable to men who secured their chemical training in German Universities.

Of the plant families known to contain essential oils the Hypericaceae have received very scant attention. It has been known for many years that the Hypericums yield a volatile oil of very unusual properties, but investigations were carried only to the point of recording some of the ordinary constants and simple chemical tests. No investigation is reported of a complete study of any oil with a view to isolating and identifying any particular constituents present. This investigation was undertaken with the purpose of securing more detailed data on the essential oil of one species of the Hypericums,—Sarothra gentianoides,—and discovering, if possible, the true nature of the constituent, or constituents, which gives to this oil its peculiar characteristics. The investigation has been pursued according to the following:

OUTLINE OF ATTACK

- I. Introduction:
  - A. Nature of volatile oils in general.
  - B. Occurrence of paraffine hydrocarbons in volatile oils.
  - C. Objects of the investigation.
- II. Historical:
  - A. A review of the literature with special reference to the following points:
    - 1. The history of this species and all other species of Hypericaceae, from the standpoint of the phytochemist and of the eclectic physician in their uses in the treatment of wounds and diseases.
    - 2. A review of investigations made on volatile oils from any species of Hypericaceae.
    - 3. Work of any kind done on this particular species of Sarothra gentianoides.
  - B. Present day adherence to the use of this herb in eclectic practice.
- III. Description and habitat of Sarothra gentianoides.
- IV. Collection and distillation of plant material:
  - A. Expert identification of the species. Location.
  - B. The collection proper of material:
    - 1. locality, 2. soil, 3. season, 4. handling of plants to insure purity of species and freedom from foreign material.
  - C. Steam distillation:
    - 1. quantity distilled, 2. time of distillation, 3. yield, 4. treatment of oil, 5. comparison of oil with other oils.
- V. Properties of the oil:
  - A. Purification of oil, B. Color, C. Odor, D. Density, E. Boiling points, F. Solubility, G. Constants, H. Elementary analysis.
- VI. Fractionation of the oil:
  - A. Preliminary,
  - B. Quantity fractionation,
    - 1. Constants on fractions.

VII. Examination for hydrocarbons:
  A. General reactions and tests.
  B. Combustion and constants.

VIII. Identification of normal nonane:
  A. Purification and fractionation,
    1. boiling range, 2. comparison with known values.
  B. Chemical properties,
    1. micro-analysis.
  C. Physical constants:
    1. molecular weight, 2. density, 3. refractive index, 4. heat of combustion, 5. freezing pt.
  D. Comparison with known constants.
  E. Synthesis of n-nonane:
    1. determination of constants,
    2. comparison with natural product.

IX. Study of oxygenated compounds:
  A. Free acids, B. Phenols, C. Aldehydes, D. Ketones, E. Esters, F. Alcohols.

X. Examination for other hydrocarbons:
  A. Olefines, B. Terpenes.

XI. Summary and conclusions.

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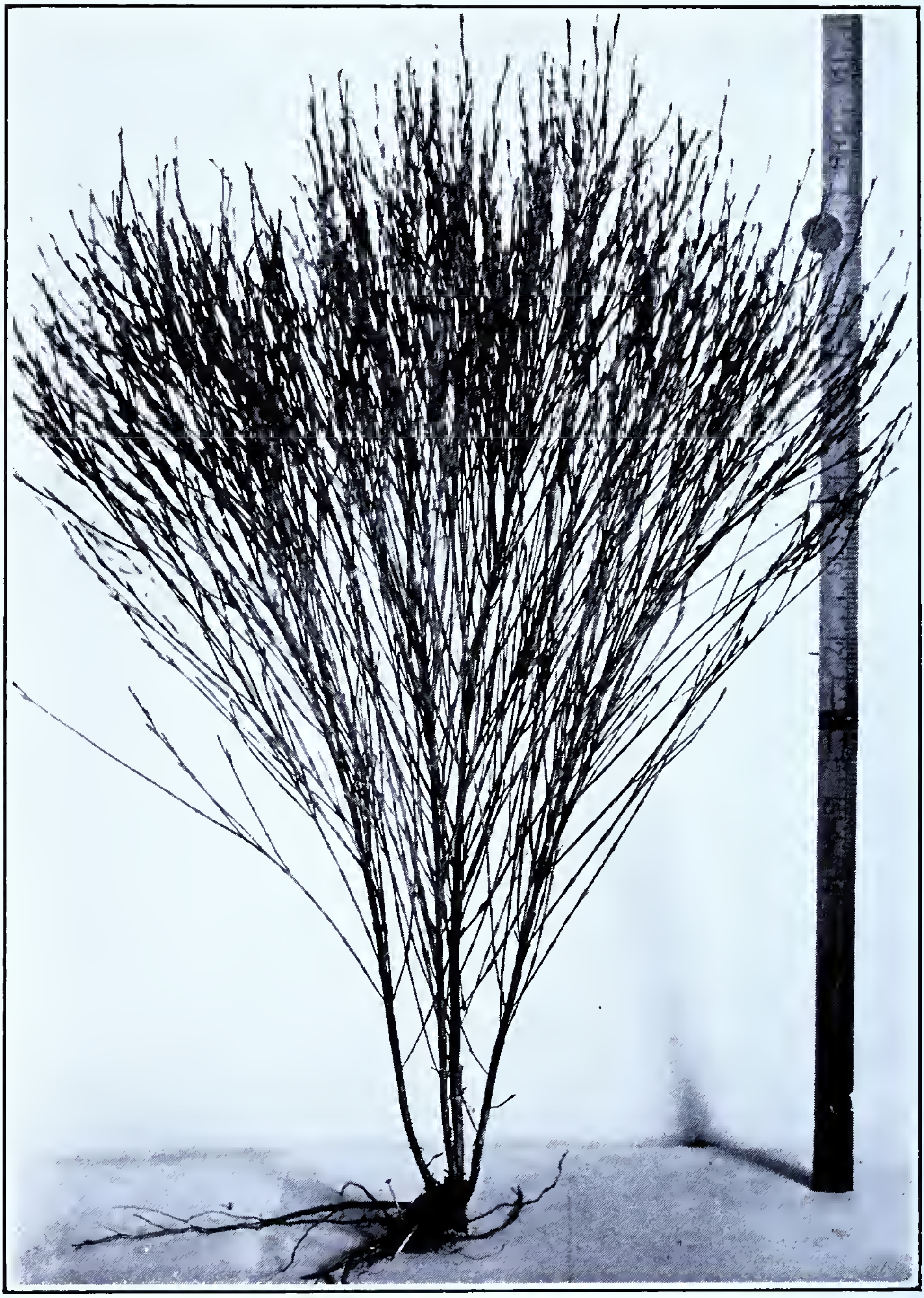


Sarothra gentianoides L., in full bloom.

THE OCCURRENCE OF NORMAL NONANE IN THE VOLATILE OIL OF SAROTHRA GENTIANOIDES L.

I. INTRODUCTION

Volatile oils, in general, are mixtures of many compounds distributed over several classes of the aliphatic, aromatic, and hydroaromatic series. Among these compounds are hydrocarbons, oxygenated substances, such as acids, alcohols, aldehydes, esters, ketones, phenols, ethers, sulfur derivatives, and even nitrogen compounds (1). While not the most important of the constituents found in volatile oils, the hydrocarbons have, perhaps, received more detailed study from the chemical standpoint. This is particularly true of the terpenes and sesquiterpenes, the study of which has been largely stimulated through the work of Semmler and Wallach.

The majority of hydrocarbons found in volatile oils belong to the alicyclic group, yet researches have revealed the presence of many hydrocarbons of the paraffine series, also. By far the majority of these belong to the solid members with melting points ranging from 10° to 80°. Some have the normal straight chain structure, while others are branched. Mostly they have a carbon content lying between C_{24} and C_{30}. Brooks mentions the occurrence of higher paraffines in rose oil, bees' wax, the resin of tobacco, the leaves of Gymnema sylvestre, in Olea europoea, Morinda longiflora, Lippia scaberrina, and in certain species of Eucalyptus (2).

Of the liquid paraffines, only the n-heptane has been definitely established as occurring in any volatile oil. This hydrocarbon has been obtained from at least three different sources,-e. g., Pinus sabiniana and Pinus jeffreyi, growing in California, and from the so-called petroleum nuts of Pittosporum resiniferum, of the Philippines (1) (2). Brooks says of this compound: "Normal heptane enjoys the distinction of being the only saturated hydrocarbon, other than the solid paraffines formed by phytochemical processes" (3).

Of more recent interest is a report of the probable presence of pentane in crude wood turpentine, but the identity of this compound has not been established (4).

More recently Miller reported the presence of a low-boiling fraction in the volatile oil of Hypericum perforatum, and states that it is most probably an aliphatic hydrocarbon not hitherto known to occur in a volatile oil (5). From a consideration of the physical and chemical properties of the fraction, the assumption is that it consists largely of an isomeric nonane. While this has not been proven, the results of our investigation on a related species lends support to the conclusions of Dr. Miller.

Miller had obtained his results at the University of Wisconsin some years prior to their publication in 1927. During the summer of 1923, the junior author of this investigation, working with Dr. Miller at the Auburn, Ala., Experiment Station, made a preliminary examination of an oil obtained from Sarothra gentianoides, and in comparing its properties with the constants secured by Miller on H. perforatum, we were at once struck with the similarity of the two. The following comparison is an interesting one:

	H. perforatum	*S. gentianoides*
Yield:	0.1146%	0.098%
Density:	0.8065 - 0.8180 (15°)	0.7665 (20°)
n_{D20}	1.4555 - 1.4612	1.4262
$(\alpha)_D$	12.4 - 15.9	6.39
A. V.	0.95	0.58
S. V.	6.88	4.43
S. V. after Acetylation:	25.07	17.35

A study of the above data reveals that values for H. perforatum are consistently higher than corresponding values for S. gentianoides. On the other hand, less than 50% of the oil of H. perforatum passes over below 150° as compared to 70% for the oil of S. gentianoides. Assuming that the low-boiling portions of these oils consist mainly of aliphatic hydrocarbons, the above differences in values are perfectly logical and exactly what one would expect to find.

So interesting were the chemical aspects of these oils that we were led to a detailed study of the oil of Sarothra gentianoides, with the primary object of ascertaining, if possible, the true nature of this low-boiling hydrocarbon. Of secondary interest was the preliminary examination of the oil for oxygenated compounds and hydrocarbons belonging to the terpene groups, with a view to their further investigation at a later date.

II. HISTORICAL

The plants belonging to the family Hypericaceae are widely distributed throughout the temperate and warm zones, being found both in the western and in the eastern hemispheres. Britton and Brown in their "Illustrated Flora of the Northern United States, Canada, and the British Possessions," state that the family contains about 10 genera and over 300 species. For the region covered in their flora, these writers list 4 genera and 26 species. Small, in his "Flora of the Southeastern United States," gives 5 genera and 43 species. The National Standard Dispensatory states that "the genus Hypericum (L) contains upwards of 200 species" (6).

Of all the genera belonging to Hypericaceae, Hypericum (L), or St. John's Wort, is the best known. But even in this genus, the literature reveals that probably only one species, H. perforatum L., has received any special study (5). Sarothra gentianoides L. (H. sarothra Michx.) has received very scant notice, indeed.

The Hypericums have been known from very early times because of their reputed medicinal properties. From this standpoint the plants seem to have acquired a rather wide notoriety, and the cures accredited to their use have been varied and numerous (7).

Many of the earliest writers upon Materia Medica have something to say about the value of Hypericum because of its curative properties. Dioscorides, a physician of the first century, a student, traveller, and voluminous writer, says that if the seed of the plant be drunk during a period of forty days, they will cure sciatica, and all aches that happen in the hips, and when drunk with wine will cure agues (8). Galen, a physician of the third century, as well as Paul of Aegina, and others, mention that it was used as a febrifuge, emenagogue, desiccative, diuretic, and vulnerary (7). Gerarde's Herball, a large volume printed in London in 1597, contains the following:

"St. John's Wort, with his flowers and seed boyled and drunken, provoketh urine, and is right good against stone in the bladder, and stoppeth the laske. The leaves, flowers, and seeds stamped, and put into a glass with oyle olive, and set in the hot sun for certain weeks together, and then strained from those herbes, and the like quantity of new put in, and sunned in like manner, doth make an oyle of the color of blood, which is a most precious remedy for deep wounds and those that are thorow the body, for sinews that are pricked, or any wound with a venomed weapon——.

"The leaves stamped are good to be laid upon burnings, scaldings, and all wounds, and also for rotten and filthy ulcers" (8).

Dr. Charles F. Millspaugh, in his book "American Medicinal Plants" (1887), gives further information regarding the use of the plant by the eclectic practitioner of more recent times. He states: "The popular and empirical uses of this plant were various, depending in great part upon its balsamic odor and property. Among the more superstitious peasantry of Middle Europe the most astonishing virtues were assigned to the herb; it became, in fact with them, a fuga daemonum and was gathered under this idea, especially on St. John's Day. It was also supposed to be useful in mania, hysteria, and hypochondriasis. Later on, especially in Eclectic practice, it became known as diuretic, astringent, nervine, and anti-hemorrhagic.

"The great use of Hypericum in wounds where the nerves are involved to any extent is the rightful discovery of the true

Science of Medicine. Dr. Franklin, who had ample field to test it during the war, says: 'Lacerated wounds of parts rich in nerves yield nicely to this drug.' Many cases of injury to the cranium and spinal column are reported benefited by its use——. It is to the nervous system what arnica is to the muscular" (7).

The National Standard Dispensatory has the following: "St. John's Wort is said to possess properties analogous to turpentine——. The recent drug may be bruised and employed as a discutient for the relief of local pains, contusions, ulcers, and bruises. It may be given internally in the treatment of chronic catarrhal conditions of the respiratory, intestinal, and urinary apparatuses" (6).

It is stated that several other species besides H. perforatum have been used in general medicine in different parts of the world. The Isle of France, - H. lanceolatum,- is considered a specific for syphilis by the natives; the Brazilian H. connatum, an astringent in sore throat; and some Russian species vaunted as cures for hydrophobia (7).

However, concerning the species Sarothra gentianoides L. (H. sarothra Michx.) the literature reveals very little. One authority states: "Sarothra gentianoides of North America, is a much-used laxative, alterative, and vulnerary, under the names of Pineweed, False St. John's Wort, Orange grass, and Nitweed" (7).

Among the older generation of inhabitants living in Catawba County, North Carolina, where the plants were gathered for this investigation, this species is still considered a valuable remedy in the treatment of kidney troubles and dropsical disorders. One old lady, seventy-five years of age, reported to the writer that her sister-in-law, during a period of pregnancy, became afflicted with a dropsy-like ailment which caused her limbs to swell and become so painful as to render her incapable of helping herself in any way. Her life was despaired of. However, as a last resort, the patient was made to drink large quantities of an infusion of the Pineweed. In a short time the swelling began to disappear and the woman entirely recovered.

III. DESCRIPTION AND HABITAT

Sarothra gentianoides L. is distributed in North America from Maine to Minnesota, and southward to Florida and Texas. It is described in books on Botany as growing in light sandy soils, but the author has found it in practically all types of soil, particularly in fields and pastures which have been allowed to lie idle for a few years, regardless of whether the soil is light sandy or gravelly, or the heavier clays. The best stand of the plants seen during the years of this investigation was located in Catawba County, North Carolina, growing along a small creek in a meadow which had been in pasture for several years. In North Carolina and Alabama, the writer has found it growing rather profusely in fields recently planted to corn and cotton. In Tennessee it has been gathered from the wheat fields after harvest.

In northern latitudes, particularly in the vicinity of New York City and northern New Jersey, the plant reaches a height of only 4 to 6 inches, but farther south, as in North Carolina, it will average 8 to 12 inches, many specimens having been collected which measured 15 inches. In the vicinity of Auburn, Alabama, the writer has found it growing to a height of 20 inches. The growth, however, depends on soil and climatic conditions. Depending on locality, the little yellow blooms appear from late July to early October.

The plant is described as follows: "Stem and bushy branches thread-like, wiry, 1-3 dm. high; leaves minute awl-shaped scales, appressed; flowers minute, mostly sessile and scattered along the erect branches; pods void-lanceolate, acute, much longer than the calyx. Sandy or rocky soil, Me. to Fla. and Tex., chiefly e. of the Alleghenies; and from s. w. Ont. to Ill., and southw." (9).

IV. COLLECTION AND DISTILLATION OF MATERIAL

The material from which the oil was obtained for this investigation was collected during the last days of August and early September, in the years from 1925 to 1929, inclusive. The collections were made in different localities, mostly northeast of the town of Hickory, Catawba County, North Carolina. The plants were pulled up by the roots and shaken to remove adhering dirt, carefully examined as to species, and all foreign matter removed. The whole fresh green herb, including tops, stems, and roots, was subjected to ordinary steam distillation in lots of about 100 lbs. for a period of 3 hours. The yields of oil separated from the distillate varied widely, from 0.072% to 0.222%, for different years. The average yield of filtered, but unwashed and undried, oil was 0.098%, based on the weight of the whole green (fresh) material.

The only other species of Hypericum to receive any attention from the standpoint of its volatile oil content is the H. perforatum. As early as 1905, Haensel reported the following data: Yield, 0.0928%; d_{20} 0.8703; angle of rotation in a 25 mm. tube in 50% chloroform solution -1° 10′; A. V. 23; S. V. 37 (10). The late Dr. Emerson R. Miller collected some of this species near Madison, Wisconsin, and reported the following constants on the distilled oil: (5).

Yields	0.106% - 0.125%
d_{15}	0.8065 - 0.8180
n_D	1.4555 - 1.4612
α_D	12.4 to 15.9

In addition to the above constants, Dr. Miller reported also the presence of α-pinene (probably), an aliphatic hydrocarbon, and one or more sesquiterpenes. Unfortunately, a complete investigation of this oil was not completed before the death of Dr. Miller. However, this author received a private communication from him before he died, and in this letter he stated that he was positive that in the low-boiling fraction would be found a nonane, probably n-nonane.

Up to the present no investigation on H. gentianoides has been reported. The results of distillations in 1926 are given in Table No. 1.

TABLE NO. I

1926 Distillations

Whole Green Plants

Date:	Wt. of Material:	Yield:	% Yield:
	Pounds	Grams	
Aug. 28th	107.0	37.0	0.077
Aug. 30th	134.0	55.0	0.090
Sept. 2nd	338.0	131.0	0.086
Sept. 3rd	232.0	97.0	0.092
Sept. 4th	328.0	126.0	0.088
Sept. 9th	106.0	54.0	0.116
Sept. 10th	189.0	62.0	0.072
Sept. 13th	214.5	90.0	0.093
Sept. 14th	244.0	119.0	0.170
	Av. % Yield		0.098

During this same 1926 season, a quantity of material was also collected and allowed to dry in a cool, dry shed, spread out in a thin layer so as not to "heat," and then distilled with results as indicated in Table No. II. Drying was from ten days to four weeks. Data gathered on separate collections of material indicated that when dried as above, the herbs lost about 70% in weight. That some oil was lost during the process of drying is proved by making calculations for percentage yield on the basis of fresh green weights. For instance, in the Table below, the plants distilled on August 20th, when calculated on the fresh green basis, show a yield of only 0.025%, and those distilled on September 28th, a yield of 0.035%, both of these figures being much below the average for fresh green material. The figures for percentages given in the Table below are based on the dry herbs.

TABLE NO. II

1926 Distillations
Whole Dry Plants

Date:	Wt. of Material:	Yield:	% Yield:
	Pounds	Grams	
Aug. 14th	39.0	14.0	0.080
Aug. 16th	89.0		
Aug. 17th	34.0	55.0	0.062
Aug. 19th	35.0		
Aug. 20th	34.0	13.0	0.090 (0.025)
Aug. 24th	23.0	11.0	0.105
Aug. 25th	87.0	48.0	0.120
Aug. 26th	43.5	24.0	0.122
Aug. 27th	77.0	32.0	0.092
Sept. 28th	45.0	24.0	0.117 (0.035)
Sept. 30th	40.0	13.0	0.072
Oct. 2nd	40.0	25.0	0.138
Oct. 7th	40.0	9.0	0.049
Oct. 13th	177.0	79.0	0.098
		Av. % Yield------	0.095

The only marked difference between the oil distilled from the dry herbs and that obtained from the fresh green plants was that the former was somewhat darker and had a more pronounced pinene odor.

During the season of 1925, distillations were also made on different portions of the plants, both fresh and dry. On August 27th, 49 lbs. of the whole fresh green herbs were collected and the bushy tops cut off, and the two portions, tops and roots, distilled separately. The 49 lbs. gave 41 lbs., or 83.6% of tops, and 8 lbs., or 16.4% of roots and coarse stems. The tops gave a yield of 50.4 grams of oil, and the roots and coarse stems only 1.7 grams. Therefore, 96% of the oil is localized in the tops of the plants, representing 83% of the mature herb.

Data on these distillations will be found in Table No. III.

TABLE NO. III

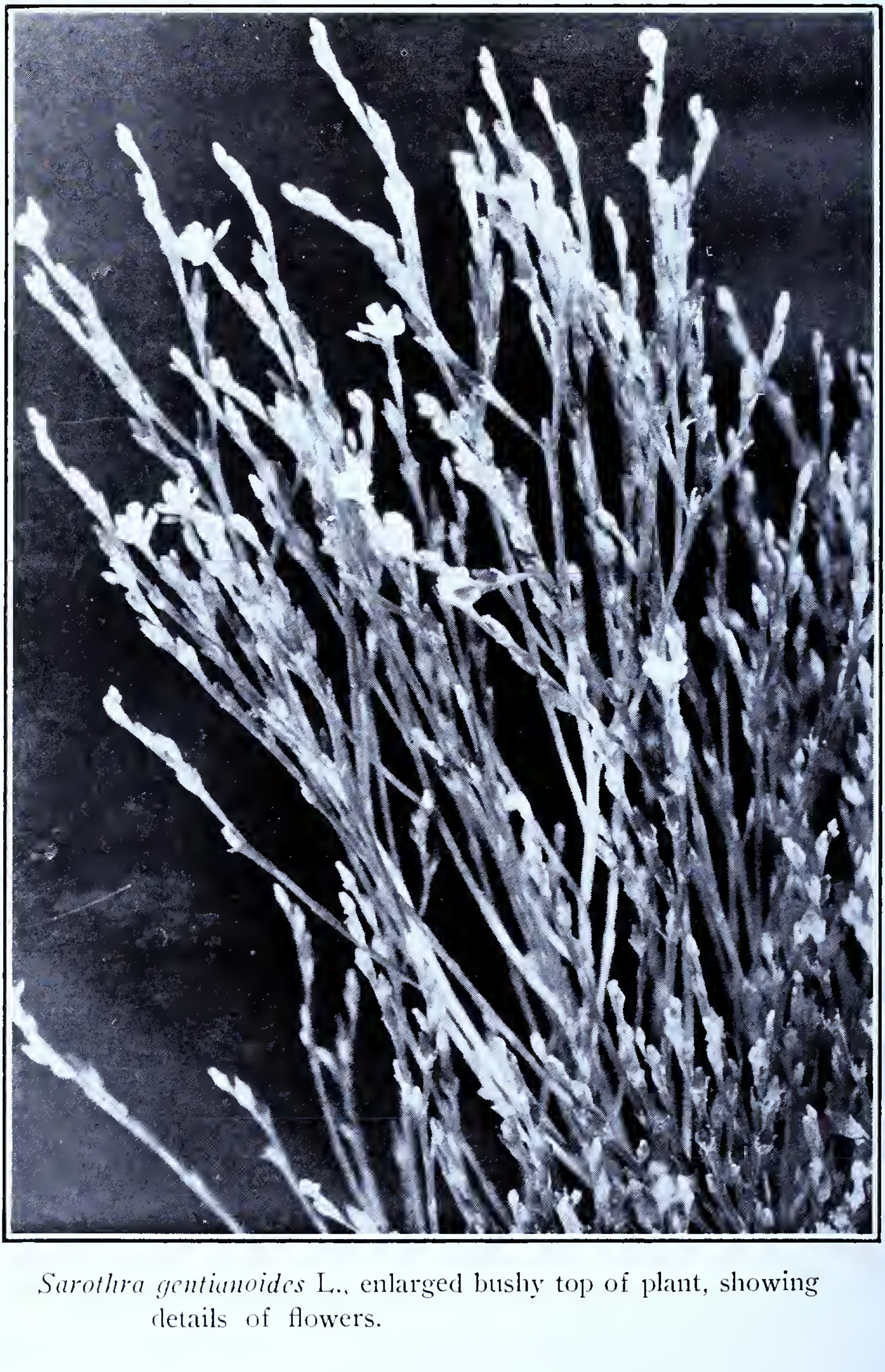
1925 Distillations

(1) Whole Green Plants

Date:	Wt. of Material:	Yield:	% Yield:
Aug. 26th	156.0 lbs.	103.0 gms.	0.145
Sept. 17th	15.0	15.0	0.220
Sept. 19th	21.0	21.1	0.222
		Av. % Yield	0.196
	(2) Green Tops Alone		
Aug. 27th	41.0 lbs.	50.4 gms.	0.217
Sept. 2nd	67.0	103.2	0.339
Sept. 18th	15.0	21.7	0.318
		Av. % Yield	0.291
	(3) Dry Tops Alone		
Sept. 17th	11.0 lbs.	13.2 gms.	0.264
Sept. 17th	10.0	8.3	0.183
Oct. 8th	9.0	12.3	0.301
		Av. % Yield	0.249

It will be noted from a study of the data given in this Table also that the yields are not uniform. However, the averages are consistently higher than in the preceding Tables. There are two possible explanations for these high yields, the most probable one being that in 1925 there was a large amount of rainfall during the growing season. This is in line with facts noted in other distillations, that the higher yields were always obtained from material gathered from low, moist meadow land. 1926 was a very hot dry summer. In the second place, the plants were distilled in smaller quantities during 1925.

A further collection and distillation of material was made during the season of 1927. In order to secure some data as to probable yield per acre when sowed to seed, a plot of one acre of light, sandy upland soil with good drainage and with an exposure to the north, was plowed and sowed broadcast with one quart of seed which had been collected in the fall of 1925. Seeding was made in the spring of 1926. The plants appeared in the spring of 1927 and were in full bloom by Au-



Sarothra gentianoides L., enlarged bushy top of plant, showing details of flowers.

gust. Due probably to an unusually dry summer in 1926, there was only what might be considered a half a stand. The plants were collected by hand picking and distilled on August 5th, 6th and 8th. The yield was 427 lbs. of fresh green herbs which gave 130.0 grams, or 0.067% of filtered oil. There were also collected from other localities during this season an additional 869.5 lbs. of material, yielding 426.5 grams, or 0.108%, of filtered oil. The largest amount of material collected during any one season was in 1929, when nearly four thousand pounds were distilled, yielding approximately two liters of filtered oil.

V. GENERAL PROPERTIES AND REACTIONS

Data secured for this investigation were obtained from oil distilled from the fresh, whole green plants, including tops, stems, and roots, principally during the season of 1929. The oil was filtered, washed with distilled water, and then dried over anhydrous sodium sulfate. The color lies in the zone of Green-Yellow, and falls between Normal Tones and Tint 1 in terms of the Bradley Color Standard. Its odor is very pleasant, and resembles that of oranges, with a slightly balsamic suggestion.

Towards ordinary solvents and reagents the oil behaves as follows: It is soluble in absolute alcohol, in ether, chloroform, and carbon tetrachloride. Cold concentrated sulfuric acid produces a yellow color, turning to a purple, and then to dark red. Cold concentrated nitric acid also produces a yellow color at first, changing to dark red, with dark particles floating between the two layers. Concentrated hydrochloric acid produces no change even on warming. Glacial acetic acid produces no change in color, but dissolves the oil. The color of the oil is not affected by either hot or cold 3N sodium hydroxide. It decolorizes neutral potassium permanganate solution. It also decolorizes promptly and completely an equal volume of a 5% solution of bromine in carbon tetrachloride. No solidification takes place at -17° C., yet the oil does take on a slightly milky appearance which clears up at +5° C.

The fuchsine and phenylhydrazine tests gave only very slight indications of the presence of aldehydes and ketones. Assayed for phenols, there was only a very slight diminution in volume.

The following constants were determined on the oil:

d^{20}_{20}	0.7665
$^{n}D_{20}$	1.4262
$(\alpha)_D$	6.39
A. V.	0.58
S. V.	4.43
Ester No.	3.85
S. V. after Acetylation	17.35

An elementary analysis of the oil revealed the presence of carbon, hydrogen, and oxygen only. A combustion gave the following results: C, 84.03%; H, 14.75%; O, 1.22%. These results show conclusively that the oil consists mainly of hydrocarbons.

VI. FRACTIONATION OF THE OIL

A preliminary fractionation of the oil was first carried out on a small portion. The acids, phenols, aldehydes and ketones, and esters, were first removed. The oil was then washed, dried over anhydrous sodium sulfate, and subjected to fractionation under a pressure of 745 mm. The results are tabulated below:

Fraction No. 1	Up to 150°	25 cc.
Fraction No. 2	150° - 160°	14 cc.
Fraction No. 3	160° - 170°	3 cc.
Fraction No. 4	170° - 200°	2 cc.
Fraction No. 5	Above 200°	5 cc.
	Residue	1 cc.

The quantity started with was 50 cc. Some liquid began to pass over at 95°, but the temperature rose rapidly to 135°, while the major portion of Fraction No. 1 came over between 146° and 150°. The most interesting feature of the oil as revealed by this preliminary distillation is that 50% of it distilled below 150°.

In the light of these results, a larger quantity of oil was fractionated, using a 4-bulb Young fractionating column. The thermometer used was a Fisher short stem, total immersion type which had been carefully checked against pure water, monobrombenzene, aniline, benzoic acid, and salicylic acid. A volume of oil amounting to 400 cc. was used, and four fractionations made. Physical data on these fractions were obtained and are tabulated in Table IV below:

TABLE NO. IV

Frac. No.	Bar. Pres.	B. P.	Density 20°/20°	n_{D}^{20}	α_D	No. cc
Whole Green Oil			0.7665	1.4262	+6.39	
1.	758 mm.	140°-145°	0.7265	1.4071	+4.05	25.0 cc.
2.		145°-150°	0.7366	1.4129	+7.52	210.0 cc.
3.	8-10 mm.	40°-60°	0.7687	1.4278	+18.96	33.0 cc.
4.		60°-110°	0.8014	1.4453	+7.46	13.0 cc.
5.		110°-125°	0.8927	1.4892	—9.77	30.0 cc.
6.		125°-140°	0.9073	1.4844	—4.75	8.0 cc.
7. Residue						15.0 cc.

The most noticeable features of the oil of Sarothra gentianoides are apparent from a study of the physical data as given in Table IV.

In the first place, the density is unusually low for a volatile oil, and very few oils have been studied with such a low figure. Even the oil from a related species, H. perforatum, is reported to have a density at 15° of 0.8065 to 0.8180 (5). An oil from Pinus sabiniana, consisting mainly of hydrocarbons of the paraffine and olefine series, has a density of 0.70 at 15° (11). The following data are interesting for comparison:

Oil of Pinus jeffreyi	0.6951
Oil of Incense Cedar	0.862
Oil of Juniper	0.8531
Oil of Sweet Orange	0.850
Oil of P. serotina	0.8478
Oil of Hops	0.840 to 0.890
Oil of Spicewood	0.855
Oil of Heracleum	0.80 to 0.88
Oil of Rue	0.833 to 0.840
Oil of Tangerine	0.853

In as much as most volatile oils have a density greater than 0.9, the above belong to oils of low density, and such oils consist largely of compounds belonging to the terpenes or derivatives of the aliphatic series. Apparently only two common volatile oils have been studied with a density lower than that possessed by the oil from Sarothra gentianoides.

Furthermore, it will be noted that 70% of the oil distilled below 150°, indicating, when considered in connection with its low density, that Fractions 1 and 2 consist mainly of derivatives of the paraffine or olefine series. Since Fraction No. 2 of Table IV represents approximately 50% of the oil, and is apparently the one in which is localized the peculiar odor of the plants, as well as the low-boiling hydrocarbon, our interest has been chiefly centered in a study of this Fraction.

VII. EXAMINATION FOR HYDROCARBONS

1. General Chemical Reactions. Portions of Fraction No. 2 were subjected to treatment with various reagents with the following results:

(a) Concentrated and fuming sulfuric acids caused some charring and a reddish coloration, with the evolution of some heat. There was very little evidence of solution or combination.

(b) Concentrated nitric acid had scarcely any action, but fuming nitric acid produced a slight increase in temperature and some resinification.

(c) The fraction was soluble in about two volumes of glacial acetic acid.

(d) A 5% solution of bromine in carbon tetrachloride was promptly and completely decolorized to an extent of two volumes of oil to one of bromine solution. There was no definite evidence of the formation of hydrogen bromide.

(e) Dilute potassium permanganate was rapidly decolorized in the cold.

(f) Metallic sodium had no action on the oil, even when warmed.

2. COMBUSTION. The Refractive Index and Bromination, as well as data secured from oxidation with permanganate, indicated the presence of a small percentage of an olefine hydrocarbon with one or more ethylene bonds. A combustion of the oil made to determine its carbon and hydrogen content was attended with unusual difficulties, owing to the explosive character of the mixture formed with oxygen. In several attempts to carry out a combustion, explosions occurred of such violence as to not only shatter the glass bulb containing the oil, but even to break the porcelain boat carrying the bulb, and blow the stoppers from the ends of the combustion tube.

The following results were obtained by Mr. M. G. Sevag, formerly Instructor at Columbia University, who, after several unsuccessful attempts to secure reliable data, finally devised a capillary tube method which worked fairly well:

Wt. of Oil:	Wt. of H_2O:	Wt. of CO_2:	%H:	%C:
0.2004 gm.	0.2729 gm.	0.6181 gm.	15.24	84.12
0.1943	0.2635	0.6015	15.27	84.43

These results indicate the presence of both paraffine and olefine hydrocarbons, and a calculation of the percentages, taken in conjunction with other physical data as given in Table No. IV, point to the probable presence of nonane, along with one of the nonylenes or an isomeric decalene in small amounts (12).

VIII. IDENTIFICATION OF NORMAL NONANE

Our interest in this oil has been primarily directed towards the isolation and identification of the low-boiling paraffine hydrocarbon. Therefore, a larger volume of the oil was treated so as to remove all oxygenated compounds and used for detailed study.

1. FRACTIONATION. A portion of the oil boiling between 146° and 152° at 735 mm. was first cut out. This was repeatedly washed with concentrated sulfuric acid until it showed no further coloration, and finally with concentrated nitric acid. It was then washed with water, dilute sodium carbonate solution, and again with water. It was finally dried over anhydrous sodium sulfate. It was then refluxed for two hours over metallic sodium, and fractionated from metallic sodium. A Young four-bulb fractionating column was employed, using a Fisher thermometer with the stem completely immersed in the vapors. A fraction was finally obtained boiling at 148.5° - 149.5° at 735 mm. pressure. A calculation based on the formula proposed by Craft,

$$dt = KT_{BO}\,(760 - P),$$

and assuming that the liquid is non-associated, would indicate a boiling range of 149.5° - 150.5° for a pressure of 760 mm. (13).

Several fractionations were made on samples of oil collected during different seasons to discover what percentage of the oil having the above boiling range would be found in the whole green oil as distilled from the plants. The percentages varied, as indicated below, from 14% to 20%.

100 cc. gave 20 cc. boiling as above = 20%
200 cc. gave 53 cc. boiling as above = 17%
360 cc. gave 55 cc. boiling as above = 15%
900 cc. gave 125 cc. boiling as above = 14%

A conservative estimate would indicate the presence in the oil of a fraction boiling between 149.5° and 150.5° at 760 mm. to an extent of 15%.

Values given for the boiling point of n-nonane vary widely, depending on the investigator. It was first produced synthetically by Krafft (14), who reported a boiling point of 149.5° at 760 mm. However, Clark and Adams (15), who prepared it by a series of steps from n-heptaldehyde, with castor oil as the source of the heptaldehyde, by condensing this with the ethyl radical by means of the Grignard reaction, give the value 150.4° - 150.6° at 759 mm. Mostly the data refer to samples of n-nonane obtained from petroleum of a variety of sources. Shepard, Henne, and Midgley have recently (16) worked on a sample of n-nonane obtained from petroleum and highly purified by the method of Shepard and Henne (17), which gave a boiling point of 150.71° at 760 mm. A fuller list of boiling point values for n-nonane is given in Table No. V.

2. Chemical Reactions. This fraction of the oil gave no reaction with potassium permanganate. It did not decolorize bromine solution. In all other respects it behaved as a saturated hydrocarbon.

It is optically inactive.

A micro-analysis made by the Research Service Laboratories, of New York, gave the following values for carbon and hydrogen:

Wt. of sample taken	3.245 mgs.
Wt. of Carbon Dioxide	10.020 mgs.
Wt. of Water	4.565 mgs.
Carbon	84.20%
Hydrogen	15.74%

Theoretical percentages for pure hydrocarbons are:

Octane: Carbon = 84.11%, Hydrogen = 15.89%
Nonane: Carbon = 84.27%, Hydrogen = 15.73%
Decane: Carbon = 84.41%, Hydrogen = 15.59%

3. Physical Constants. A series of molecular weight determinations was made on the fraction with the following results: (a) 131.1, (b) 129.3, (c) 130.6, (d) 128.8. The average of these is 129.9, while the value for nonane based on the latest International Atomic Weights would be 128.2. Values a, b, and c above were obtained by the Freezing

Point Method, using benzene as a solvent, while d was obtained by the Vapor Density Method (18).

Density determinations on the fraction made at 20° and referred to water at 20°, using a pycnometer of the type as described by Findlay (19), gave the following values: (a) 0.7166, (b) 0.7192, (c) 0.7169, (d) 0.7179, or an average of 0.7177. Krafft (14) reported a density for synthetic n-nonane of 0.7177 at 20° referred to water at 4°, and Reid gives the same value (20). Shepard, Henne and Miggley report the value 0.71780 at 20° referred to water at 4° (16). For other values, reference is made to Table No. V.

The Refractive Index, as determined by means of an Abbe Refractometer at 25°, was found to be 1.4025, while reported values are 1.405 (21), 1.4165 (22), and 1.40340 (16).

Through the courtesy of Professor E. E. Randolph, of the Department of Chemical Engineering, North Carolina State College, a determination on the heat of combustion was made, using a Parr Bomb Calorimeter, the value found being 1,448,248 calories. The calculated value for n-nonane is 1,462,300 calories.

A determination made in the laboratory of Dr. H. D. Crockford, of the Department of Physical Chemistry, University of North Carolina, showed the freezing point to be —60°.

The author is very much indebted to the above named gentlemen for their kindness in obtaining the data mentioned.

All of the above data on the fraction of oil under consideration are tabulated in the following Table No. V.

TABLE NO. V

B. P. 760 mm.	F. P. °C	Density	$n_{D_{25}}$	α_D	Heat of Combust.	Molec. Wt.	%C	%H
Experimental Values								
149.5—150.5	—60	0.7177 20°/20°	1.4025	±0	1.488 Cal.	129.9	84.20	15.74
Reported Values								
149.5 (14)	—51 (21)	0.7177 (14)	1.405 (21)		1.462	128.2	84.27	15.75
149—	—53.68 (16)	0.7219^{15}_{15} (15)	1.4165 (22)					
151 (22)		0.7177 (20)	1.40340 (16)		(These values are calculated)			
149 (23)		0.718 (21)	1.4025 (15)					
150—150.6 (21)		0.7348 (22)						
150.2—150.9 (24)		0.7380 (24)						
150.71 (16)		0.717 (23)						
150.4—150.6 (15)		0.7178^{20}_{4} (16)						

Data on the nonanes are meagre. Of the 35 isomers possible for nonane, only 10 have been reported (25). The physical constants for those which have been reported are few and uncertain. The normal nonane has received by far the greater attention, and the data are more dependable. However, the above values reveal that results obtained from the fraction of oil under consideration agree closely with such constants as appear in the literature, and leaves little doubt as to the identity of normal nonane.

In nature, n-nonane has been reported along with n-decane in petroleum of the Pennsylvania type (26), and from the Cabin Creek Field, of West Virginia (24). It has not yet been reported in any essential oil.

EXPERIMENTAL

1. Synthesis of n-Nonane. In order to compare the properties of that fraction of the oil believed to be n-nonane with nonane of known structure, an attempt was made to prepare pure n-nonane. The first effort was directed to the Wurtz reaction. Pure n-amyl bromide and pure n-butyl bromide, in ether solution, were treated with metallic sodium in small quantities at a time, in the proportions of one mole each of the halides and two moles of sodium. After the reaction was complete, the ether solution was filtered, washed, and dried over anhydrous sodium sulfate. It was then subjected to fractional distillation, when a small quantity of material boiling between 149° and 150° at 760 mm. pressure was obtained which agreed closely in physical properties with the constants given for n-nonane. However, due to side reactions, presumably with the formation of octane and decane, and the difficulty experienced in getting a good separation, this method was abandoned.

The method finally adopted was suggested by Mr. R. E. Marker, now of the Rockefeller Institute, and was essentially the process used by Chavanne (27), with certain minor modifications. This consisted in condensing two radicals by means of the Grignard reaction, the starting materials in this particular synthesis being ethyl bromide and n-heptaldehyde. The resulting n-hexyl ethyl carbinol was then dehydrated and the nonylene hydrogenated to nonane.

The ethyl bromide used was a commercial product carefully purified by first shaking with concentrated sulfuric acid, then washing with water, dilute sodium carbonate solution, and again with water. It was finally dried over calcium chloride and distilled. The portion passing over between 38° and 39° at 760 mm. pressure was employed for this work.

The n-heptaldehyde was obtained from the Eastman Kodak Co. It was dried over sodium sulfate and subjected to fractional distillation. The fraction boiling between 155° and 156°, and having a density of .82 was used for this synthesis.

The Grignard reagent was prepared by treating 65 grams magnesium with 425 grams ethyl bromide in twice its volume of absolute ether. To this was added, with constant stirring while the flask was surrounded with ice water 400 grams of the n-heptaldehyde, also dissolved in absolute ether. The mixture was allowed to stand over night and then poured on ice water. The white precipitate was dissolved in the calculated amount of 10% hydrochloric acid sufficient to decompose the magnesium compound, the ether layer separated, dried over anhydrous potassium carbonate, the ether distilled off, and the residue fractionated.

The fraction boiling between 192° and 194° was then mixed with the calculated amount of red phosphorous and iodine sufficient to replace the hydroxyl group with iodine and heated on the steam bath for two hours. It was filtered, washed, and refluxed for one hour with an excess of strong alcoholic potassium hydroxide. The alcohol was distilled off, the resulting liquid poured into a large volume of cold water when the nonylene separated out on top. This was removed, washed, dried over calcium chloride and distilled from metallic sodium. A fraction boiling at 149.4° - 149.9° was collected for final reduction.

The reduction of the nonylene was accomplished by passing its vapor mixed with hydrogen over freshly reduced nickel at a temperature of 160°.

The nonane was washed repeatedly with concentrated sulfuric acid, followed by concentrated nitric acid, until no further coloration of the acid was observed. It was then washed with water, dilute sodium carbonate solution, followed by a further washing with water, dried over sodium sulfate. It was refluxed for two hours over metallic sodium, and finally fractionated from sodium. The fraction boiling between 149.5° and 150.5° at 760 mm. was collected for the determination of constants for comparison.

Due to side reactions and the probable formation of isomers, the final yield was uniformly small in a number of runs. The literature reveals no better method for the synthesis of n-nonane.

2. Physical Constants. The following constants were determined on the synthetic n-nonane:

Boiling range (760 mm.)	149.5° - 150.5°
Density 20°/20°	0.712
Freezing Point	—51°
Refractive Index at 25°	1.4055

A mixed boiling point obtained from the natural and the synthetic products gave negligible difference.

B. PART TWO

As stated elsewhere in this article, our chief interest in the investigation of the oil of Sarothra gentianoides has been directed towards the separation and identification of the paraffine hydrocarbon n-nonane. Yet the oil presents other features of interest from a chemical standpoint. In the course of our investigation, we have had occasion to make some preliminary studies on that portion of the oil remaining after the removal of the nonane fraction, and while our results are not conclusive in all cases, they are of sufficient interest to warrant further investigation on the oil, and this is planned for the near future.

This portion of our work has been directed along two different lines: First, a study of oxygenated compounds, and second, a study of the hydrocarbons.

I. OXYGENATED COMPOUNDS

1. Free Acids. A quantity of the oil amounting to 750 cc. was shaken with a 3% solution of sodium bicarbonate. The bicarbonate solution was separated, concentrated to small volume, acidified with dilute sulfuric acid to liberate the organic acids and these removed with ether. Upon evaporating the ether there resulted a small quantity of a dark-brownish oily material with an odor suggestive of rancid butter. This was taken up with dilute sodium hydroxide and a silver salt formed. Upon drying and igniting the following results were obtained:

Wt. of silver salt taken	0.5340 gm.
Wt. of silver left	0.0265 gm.
% of silver found	49.63

The silver salt of valeric acid contains 51.64% silver, and the silver salt of caproic acid contains 48.39%. Since there was some darkening of the silver salt, indicating slight decomposition with an increase in the percentage of silver, the conclusion is that caproic acid is present.

2. Phenols. After removing the acids, the oil was again shaken out with a 3% solution of potassium hydroxide to remove phenolic bodies. This alkaline solution was acidified

with dilute sulfuric acid and extracted with ether. From this treatment there was obtained a small quantity of a brownish, jellylike, oily substance resembling dirty vaseline. From this was prepared an ester of 3.5-dinitrobenzoic acid according to the method proposed by Phillips and Keenan (28). This gave a melting point of 207° (uncor.), but the results were inconclusive.

3. ALDEHYDES. Aldehydes were removed from the oil by means of saturated sodium bisulfite solution. This was decomposed with sodium carbonate, and the aldehydes removed with ether. An oily substance was obtained which was converted into a semicarbazone. This melted at 105° - 106°.

4. KETONES. The original oil showed a faint test for ketonic bodies. An attempt was made to prepare a derivative by treating the oil with semicarbazide hydrochloride. After standing for three days some crystals separated which gave a melting point of 231° - 232°. The semicarbazone from camphor melts at 236° - 238°.

5. ESTERS. The Saponification Value obtained in the preliminary study of the oil, showed the presence of a small percentage of an ester. A quantity of the oil was saponified, after removing the acids, aldehydes, and ketones, with N/2 alcoholic potassium hydroxide. The alkaline solution was concentrated to small bulk. It was acidified with dilute sulfuric acid and steam distilled. The distillate had an acid reaction, and from it was prepared a silver salt. Upon ignition there was obtained 41.69% silver. The silver salt of caprylic acid contains 41.67% silver.

6. ALCOHOLS. The quantities of the foregoing compounds appeared to be insufficient to account for all oxygenated bodies in the oil. Therefore, an attempt was made to locate terpene and alicyclic alcohols in the higher fractions of the oil. From Fraction No. 5 as given in Table IV, there was prepared according to the method of Wallach (29) a nitroso-chloride which melted at 106.5°. The melting point of the nitroso-chloride for α-terpineol is given as 107° to 108°. The odor

and other properties of this fraction agree fairly well for those recorded for the liquid l-α-terpineol.

Fraction No. 6 was treated with Beckmann's Chromic Acid Mixture (30), when there was immediately observed the odor of citral. The oily product behaved in exactly the same way towards Schiff's reagent as pure citral. The constants for this fraction agree fairly well with those recorded for geraniol, and the conclusion is that this compound is very probably a constituent of the oil.

II. HYDROCARBONS

Our second line of investigation on the portion of oil remaining after the removal of n-nonane, has been in connection with a study of the other classes of hydrocarbons present. In a general way the nature of these hydrocarbons may be deduced from the data given in Table No. IV. Fractions 1, 2, and 3 should consist mainly of derivatives of the paraffine and olefine series. Terpenes and sesquiterpenes, if present, would likely be found in the remaining fractions.

1. Olefines. The fraction of the oil from which the normal nonane was removed represents more than 50% of the total. Its chemical behavior showed conclusively that it contains an unsaturated compound. It decolorizes permanganate and absorbs bromine.

In order to secure information as to the nature of this unsaturated compound, or compounds, an attempt was made to oxidize the olefines to acids for their identification.

Portions of the fraction were subjected to vigorous oxidation with potassium permanganate, filtered, the unchanged oil separated, the alkaline liquid acidified with dilute sulfuric acid, and steam distilled. From the distillates there were prepared silver salts which gave the following results on ignition:

(a) Ag = 42.00%
(b) Ag = 41.17%
(c) Ag = 42.28%
(d) Ag = 41.17%

Caprylic acid contains 41.67% metallic silver.

From the above distillate there was also prepared a sodium salt, the water solution of which was optically active, the value being, $(\alpha)_D = -15.8$.

A further portion of the oil was subjected to oxidation by means of chromic acid. From the oxidation products, there was prepared a silver salt, giving 52.19% metallic silver. The silver salt of valeric acid contains 51.64% metallic silver.

The conclusion to be drawn from the oxidation of Fraction No. 2, is that it yields two different acids, probably active caprylic and valeric acid. These two acids could be formed from a single olefine hydrocarbon of thirteen carbons, assuming a single olefine linkage, or from two different hydrocarbons, one of which would give the active caprylic acid, and the other the valeric acid. In the light of the physical data obtained on the Fraction, one is led to conclude that the latter is more probable.

2. TERPENES AND SESQUITERPENES. No definite attempt has yet been made to separate and identify any hydrocarbon in the higher fractions of the oil. The very nature of these hydrocarbons makes further investigation necessary for their identification, and this work is planned for the near future.

SUMMARY

1. The distinct contribution of this investigation lies in the fact that from the volatile oil of Sarothra gentianoides there has been isolated and identified normal nonane to the extent of approximately 15%.

2. The oil consists mainly of low-boiling hydrocarbons.

3. In addition to n-nonane, there are also present in the oil the following compounds:
   - (a) Caproic acid.
   - (b) Caprylic acid, in the form of its ester.
   - (c) Geraniol.

4. There is also strong evidence of the presence of the following substances:
   - (a) A low-boiling, optically active olefine hydrocarbon.
   - (b) Terpineol.
   - (c) An aldehyde.
   - (d) A ketone.
   - (e) Terpenes.
   - (f) Sesquiterpenes.

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VITA.

Simon J. Marion was born near Bristol, Tennessee, November 16, 1888. After completing his High School course, he was graduated from Roanoke College, Salem, Virginia, in June, 1913, with the A. B. degree.

He was a graduate student at Princeton University during the year 1913-14.

From 1914 to 1918 he was teacher of science in the Raleigh, North Carolina, High School. He was instructor in chemistry in the North Carolina State College from 1918 to 1921.

During the year 1921-22 and the summer of 1922, he was a graduate student at Columbia University. From September, 1922, to September, 1923, he was Assistant Research Chemist at the Alabama Experiment Station. Since 1923, he has been holding the position of Professor of Chemistry at Lenoir Rhyne College, Hickory, N. C.

He did additional graduate work in chemistry at Columbia University during the summer of 1925, and during the spring semester of 1928.